



(12) UK Patent (19) GB (11) 2 090 603 B

SCIENCE REFERENCE LIBRARY

(54) Title of invention

Water soluble films of partially hydrolysed
polyvinyl acetate and polyacrylic acid

(51) INT CL³; C08L 29/04 33/02 // C08J 5/18

(21) Application No
8137743

(22) Date of filing
15 Dec 1981

(30) Priority data

(31) 216358

(32) 15 Dec 1980

(33) United States of America
(US)

(43) Application published
14 Jul 1982

(45) Patent published
5 Sep 1984

(52) Domestic classification
C3M 112 120 122 123 200 XA
U1S 1814 3029 1366 3045 3039
3069 C3M

(56) Documents cited
GBA 2065127
GB 1586494
GB 1575928
GB 1308155
GB 1256761
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GB 0854987

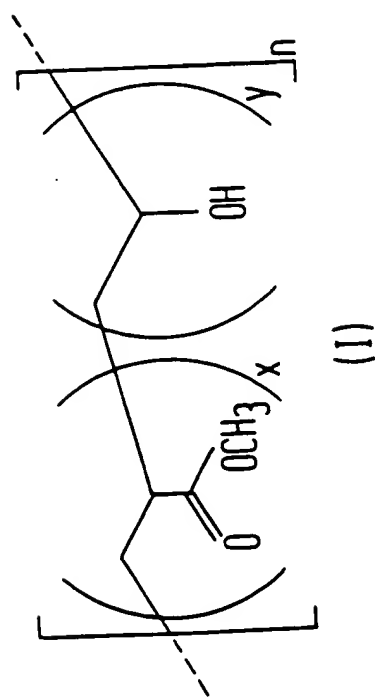
(58) Field of search
C3M
C3V
C3J

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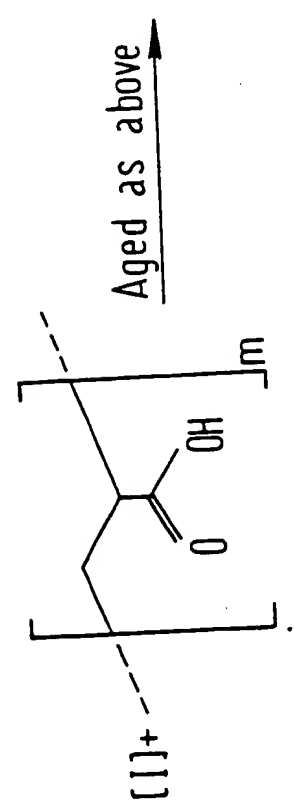
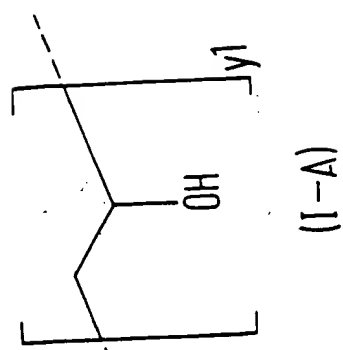
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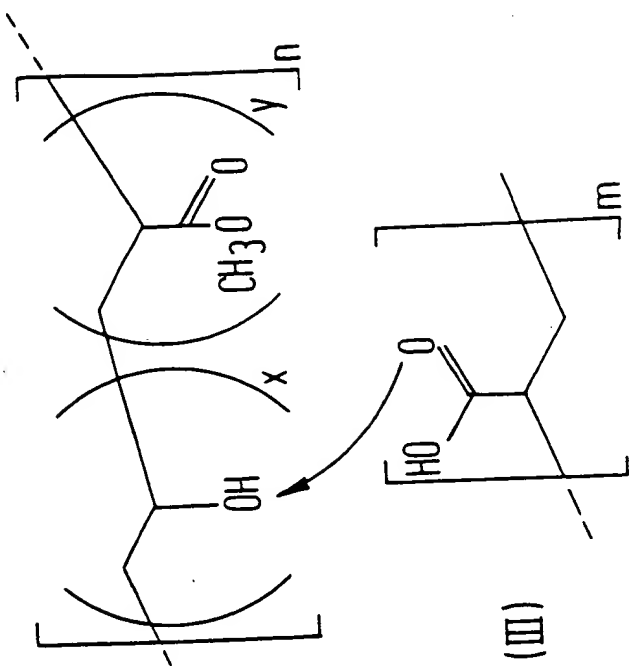
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High Temperature,
high R.H.
or in presence
of alkali



Aged as above



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WATER SOLUBLE FILMS OF PARTIALLY
HYDROLYSED POLYVINYL ACETATE AND
POLYACRYLIC ACID

This invention relates to water soluble films. More particularly, this invention relates to water soluble films useful in packaging applications, especially for dry detergents and similar water soluble commodities, formed from homogeneous blends of water soluble partially hydrolysed polyvinyl acetate and polyacrylic acid.

Packaging materials formed from film-forming materials which are water soluble have been used for many years for packaging water soluble or dispersible dry, solid materials which may be toxic or otherwise harmful to the user or which may be difficult to weigh out in accurate portions, or simply for the convenience of the user. Examples of typical materials used in aqueous environments which have been packaged or proposed for packaging in water soluble films include, for example, cleaning products, such as laundry detergents, bleaches and caustic cleansers; pesticides, such as herbicides, fungicides, insecticides, and nematocides which are applied as aqueous sprays; and various other pulverulent water soluble or dispersible chemicals, such as carbon black, pigments and dyes, and food products.

One of the most widely investigated water soluble film-forming materials used or promoted for packaging of such powdery materials is polyvinyl alcohol (made by hydrolyzing polyvinyl acetate). At hydrolysis levels of up to about 97-99%,

partially hydrolyzed polyvinyl acetate is soluble in water although the rates of dissolution are too slow to be practical, especially in cold water. Partially hydrolyzed polyvinyl acetate is frequently referred to as polyvinyl alcohol.

5. Many attempts have been reported in the patent literature to improve upon the properties of water soluble "polyvinyl alcohol" packaging films. These efforts have included, for example, selection of special plasticizers, e.g., U.S. Patent 2,948,697 - J.A. Robertson and U.S. Patent 3,106,543 - J.N. Milne, assigned to E.I. duPont de Nemours; U.S. Patent 3,157,611 - M.K. Lindemann, assigned to Air Reduction Co.; U.S. Patent 3,374,195 - T.S. Bianco et al., assigned to Mono-Sol Div. of Balfin-Montrose Chemical Co.; modification or copolymerization of the polyvinyl alcohol, e.g., U.S. Patent 3,300,545 - R.L. Baechtold, assigned to American Cyanamid, U.S. Patents 3,441,547 and 3,505,303 - M.K. Lindemann, assigned to Air Reduction Co., U.S. Patent 3,277,009 - M. Freifeld, et al., assigned to General Aniline & Film Corp. and blending polyvinyl alcohol with other polymers, e.g., U.S. Patent 2,850,741 - I.M. Klein, U.S. Patents 3,695,989 and 3,892,905 - R.E. Albert, assigned to E.I. duPont de Nemours.
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30. However, none of these efforts have been entirely satisfactory in providing films which are sufficiently stable against degradation of physical properties when stored under relatively low humidity/low temperature or relatively high humidity/high temperature conditions. Thus, at low humidity/low temperature conditions, many of the films become brittle and lose elasticity, resulting in loss of impact resistance and tear strength. They may also lose their clarity and

- heat sealability. At high humidity/high temperature conditions (e.g. 100°F (37.8°C) and 80% R.H.) the degree of hydrolysis of the partially hydrolyzed polyvinyl acetate may increase to levels at which the partially hydrolyzed polyvinyl acetate is no longer water soluble or the film may simply become too soft and tacky to be stored or handled. The films may become water insoluble after only 2 weeks at these conditions. For this reason, it is usually necessary to store the films under specially controlled atmospheric conditions or to provide special waterproof protective release films between plies of the water soluble partially hydrolyzed polyvinyl acetate films, as shown, for example, in Albert- U.S. Patent 3,892,905, at Col.3, line 47 to Col. 4, line 4 and Col. 4, lines 44 to 54. Many of the prior art films suffer from poor aging stability when in contact with alkaline substances, even under moderate (e.g. 50% R.H.) humidity conditions. For example, they may become water insoluble after only 2 to 3 weeks.
- Partially hydrolyzed polyvinyl acetate is not fully compatible with most polymers and, therefore, does not form completely homogeneous blends and, accordingly, it is difficult to form uniformly transparent and mechanically strong films. Still further, the prior art films do not have sufficiently high rates of dissolution in water, particularly cold water, i.e., at water temperatures below about 60°F (15.6°C) especially at or near ice water conditions.

Accordingly, it is an object of this invention to provide water soluble films, useful for packaging applications, which have high rates of solubility

in both cold and hot water.

It is a further object to provide water soluble films which are of reduced sensitivity to humidity.

5. A further object of the invention is to provide water soluble films which are clear, transparent, non-tacky, easily handleable, heat sealable, and mechanically strong and which are inexpensive to produce.

10. According to the present invention a water soluble clear transparent coherent self supporting film suitable for use in packaging comprises a uniform homogeneous mixture of water soluble partially hydrolyzed polyvinyl acetate and polyacrylic acid.

15. Generally, the polymers are blended at weight ratios (on a dry solids basis) of partially hydrolyzed polyvinyl acetate to polyacrylic acid in the range of from about 10:1 to 1:1. The partially hydrolysed polyvinyl acetate preferably has a degree of hydrolysis
20. of less than about 96% and more than 79% and a molecular weight in the range of about 10,000 to about 50,000 (weight average molecular weight). Typically, the degree of hydrolysis may be in the range 85% to 95% and the molecular weight in the range 20,000
25. to 40,000; particularly preferred ranges are 85% to 90% for the degree of hydrolysis and 22,000 to 31,000 for the molecular weight. The polyacrylic acid is preferably a homopolymer of acrylic acid having a molecular weight in the range of from about 30,000
30. to about 400,000 (weight average molecular weight), preferably in the range of from 50,000 to 300,000 (weight average molecular weight).

Small amounts of one or more plasticizers to lower the glass transition temperature, T_g , and

- brittle temperature, T_f , and one or more nonionic anti-foaming agents to suppress foaming during film formation are desirably included in the polymer blend. In addition, in view of the biodegradability of the water soluble films, a biocide can be included in the film-casting solutions with the polymers and other adjuvants.
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- The water soluble films of this invention are especially suitable for packaging pulverulent or powdery or other solid dry materials which are to be dissolved or suspended in aqueous solutions for use. These films are useful for packaging any dry commodities where rapid water solubility, even at ice water temperatures, is required and especially where continued stability to aging at high and low temperatures and humidities and good strength are required. For example, a premeasured quantity of a powdery laundry detergent can be stored in a sealed bag made from the water soluble films and simply dropped into the washing machine. The film package will rapidly dissolve upon coming into contact with the wash water to release the detergent. There is no residue from the bag which could clog pipes, valves or other components of the washing machine or other apparatus with which the films are used. The polymer materials are also biodegradable and therefore do not pose any environmental pollution problems.
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- The films can be simply prepared by forming an aqueous solution of the partially hydrolyzed polyvinyl acetate and polyacrylic acid and laying down the solution on a smooth casting surface. A doctor blade or other means can be used to obtain the desired film thickness. Upon evaporation of the aqueous solvent, a clear transparent and uniformly thin film of the polymer blend is left which can be easily stripped from the casting surface.

- The casting surface can be any smooth, hard material such as steel, aluminium, glass or a polymer, e.g. polyolefin, polyester, polyamide, polyvinyl chloride, polycarbonate, or polyhalocarbon. The rate of evaporation of the aqueous solvent can be
5. increased by heating the casting surface or by exposing the deposited coating solution to, for example, heated air or infra-red rays. The casting surface may be flat or the film may be made on standard (drum type) industrial film casting machinery
 10. followed, for example, by oven drying.

- The aqueous coating or casting solution can be formed by any desired means. For example, the partially hydrolyzed polyvinyl acetate can first be dissolved in water and the polyacrylic acid added
15. to this solution.

- The partially hydrolyzed polyvinyl acetate can be added to a solution of polyacrylic acid. Alternatively, the two polymers can first be blended together and then added to water. The choice
20. of any particular method will generally be dictated by the form of the commercial source of the respective polymers. Thus, if partially hydrolyzed polyvinyl acetate is purchased in the form of an aqueous solution and the polyacrylic acid as a powder or
 25. pellets then the first mixing method will be most expedient.

- However, it has been found that with typical commercially available granular, partially hydrolyzed polyvinyl acetate, the best results are achieved by
30. preparing the polymer blend casting solution by first dissolving the granules in water by a two step procedure: adding the granules to cold to room temperature or warm water to form a dispersion, and then heating the solution at an elevated temperature
 35. in the range of about 150°F to 250°F, (65.6 to 121°C) preferably 180°F to 200°F (82 to 93°C) with vigorous agitation. To prevent foaming with possible occlusion

of air bubbles in the cast film, an anti-foam agent is preferably added to the solution before raising the temperature and agitating.

Any anti-foam agent which will not adversely effect the water solubility of the film can be used.

5. Non-ionic surfactants are useful anti foam agents. For example, the polyalkylene oxide condensates of alkylphenols and alkylene oxide condensates with a hydrophobic base are suitable classes of nonionic surfactants. As typical examples of the former class,
 10. mention can be made of the condensation products of alkyl phenols having an alkyl group containing from about 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with about 5 to 25 moles of ethylene oxide per mol of alkyl
 15. phenol. A typical example of the latter class is a condensation product of ethylene oxide and/or propylene oxide with propylene glycol.

- The water soluble condensation products of aliphatic alcohols having from 8 to 22 carbon atoms,
20. in either straight chain or branched chain configuration with alkylene oxide, e.g. a coconut alcohol-ethylene oxide condensate having from about 5 to about 30 mols of ethylene oxide per mol of coconut alcohol (e.g., C_{10} - C_{14} alcohol fraction),
 25. are also useful non-ionic surfactant anti-foaming agents.

- Specific examples of non-ionic anti foaming agents include ethoxylated octyl and nonyl phenol containing 5 to 12 mols ethylene oxide and available
30. commercially under such tradenames as TRITON CF-32

TRITON X-100, TRITON X-45, STEAROX DJ and IGEPAL; and the polyoxyalkylene alcohols such as those sold commercially under the PLURONIC trademark. The work TRITON is a trademark.

5. In addition, the silicone emulsion anti-foaming agents, such as Antifoam AF, and others, available from Dow Chemical Company, can be used.

The amount of the anti-foam agent is not especially critical and generally only that amount

10. which is effective to suppress foaming of the partially hydrolyzed polyvinyl acetate during the preparation of the film casting solution will be used. Amounts in the range of from about 0.005 to 1.0%, preferably from about 0.05 - 0.5% by weight, based on partially
15. hydrolyzed polyvinyl acetate solids, is satisfactory. For example, with Triton CF-32 about 0.1% of anti foam agent is sufficient.

The solid loading content of the aqueous coating solution will be selected based on the desired viscosity and on the desired film thickness. Generally,

20. solid contents in the range of from about 5% to about 30%, preferably from about 8% to about 20% more preferably from about 10% to about 15%, and film thicknesses in the range of from about 0.00005
25. inch (0.0127 mm) to about 0.010 inch (0.254 mm) preferably from about 0.001 (0.0254 mm) to about 0.005 inch (0.127 mm) and more preferably from about 0.001 inch (0.0254 mm) to about 0.002 inch (0.051 mm) are satisfactory. Naturally, it is preferable to minimize
30. the amount of solvent as much as possible so that the time required for drying the deposited film will be minimized.

Any of the commercially available forms of water soluble partially hydrolyzed polyvinyl acetate are suitable for use in the invention. Generally, degrees of hydrolysis wherein 99% or more of the acetate groups of polyvinyl acetate are replaced by hydroxyl groups are not water soluble, while above 96% hydrolysis, the rates of solubility may be too low or solubility in cold water may be impaired. On the other hand, at hydrolysis levels below about 85%, especially below about 79%, the polymer is not sufficiently soluble. Accordingly, partially hydrolyzed polyvinyl acetate having a degree of hydrolysis of from about 79% to about 95%, preferably from about 85% to 90%, especially preferably from about 86% to 89% is preferably used as the water soluble partially hydrolyzed polyvinyl acetate component of the polymer blend.

The partially hydrolyzed polyvinyl acetate should have a molecular weight sufficiently high to render it capable of forming a coherent self-supporting film but not so high that it does not dissolve or that it forms a gel when added to water. Generally, the partially hydrolyzed polyvinyl acetate is selected to have a molecular weight (weight average) in the range of from about 10,000 to about 50,000, preferably from about 20,000 to about 40,000, and more preferably from about 22,000 to 31,000.

The other essential component of the polymer blend is preferably a homopolymer of acrylic acid. Again, any of the commercially available forms of polyacrylic acid have been found to be compatible with and form homogeneous solutions and blends with partially hydrolysed polyvinyl acetate.

5. For purposes of degree of solubility in cold and hot water, and rate of solubility, the polyacrylic acid should have a molecular weight in the range of from about 30,000 to about 400,000, preferably from about 50,000 to about 300,000, especially from about 100,000 to about 200,000.

10. The partially hydrolyzed polyvinyl acetate and polyacrylic acid are preferably blended with each other to provide weight ratios (on a dry matter basis) in the range of from about 10:1 to about 1:1, preferably from about 6:1 to about 2:1, more preferably from about 5:1 to 3:1, and especially about 4:1.

15. The properties of the water soluble films of the invention can be further improved by incorporating any of the known plasticizers for partially hydrolyzed polyvinyl acetate into the aqueous casting solutions. In particular, the glass transition temperature, T_g , and brittle temperature, T_f , is lowered so that
20. the impact strength of the film, and hence packages produced therefrom which are subject to low temperatures and humidities are greatly improved. The preferred plasticizers include polymerized glycerol (e.g. Dow Chemical Co.'s Polyglycerol W-80) and glycol
25. ethers, (e.g., tetraethylene glycol). Other suitable plasticizers include, for example, glycerol, diethylene glycol, triethylene glycol, polyethylene glycol, and other ether polyols, triethanolamine, 1,3-butanediol, CARBOWAX-2000 (Trade Mark), triethanol-
30. amine acetate, ethanol acetamide, as well as the plasticizers mentioned in any of the above mentioned patents. Mixtures of plasticizers can also be used.

5. The amount of the plasticizer can vary widely. Generally, the plasticizer will be added to the aqueous casting solution in amounts sufficient to provide about 0.5% to about 5%, preferably about 1% to about 4%, more preferably about 2% to 3% by weight, based on the weight of the entire casting solution. In terms of total polymer (partially hydrolyzed polyvinyl acetate plus polyacrylic acid) content of the water soluble film, the amount of the plasticizer in the film is preferably from about 10% to 30%, more preferably from about 15% to about 25% by weight.

10. In view of the biodegradability of the partially hydrolyzed polyvinyl acetate and polyacrylic acid components, it is often desirable to include one or more biocides, especially bactericides, in the water soluble film. Generally, the biocide will be the last component added to the casting solution. The amount of biocide is not particularly critical, and will depend on the amounts of the polymers and on the particular biocide. Generally amounts up to about 0.1%, based on the amount of the partially hydrolyzed polyvinyl acetate solids will be sufficient.

15. Any conventional bactericide can be selected so long as it is compatible with the polymer blend. The biocide should be non-toxic to humans, especially for those applications of the water soluble films, such as packaging films for detergents and other cleaning agents, or for foodstuffs, where there is a possibility that the components of the film, when dissolved, will come into contact directly or

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indirectly, with the skin, or may even be consumed.

Examples of suitable water soluble bacteriostatic agents include, for example Alkyl (C_8-C_{18}) di-lower alkyl

5. benzyl ammonium chlorides, Di-isobutyl phenoxxy ethoxy ethyl dimethyl benzyl ammonium chloride, monohydrate, Alkyl (C_9-C_{15}) tolyl methyl trimethyl ammonium

- chlorides, Cetyl pyridinium chloride or bromide, N-myristyl benzyl-N, N-diethyl-N-ethanol ammonium chloride, Alkyl (C_8-C_{18}) dimethyl ethyl benzyl ammonium chlorides, Lauryl isoquinolinium bromide, 10. Alkenyl dimethyl ethyl ammonium bromides, N(methyl heptyl-colamino-formyl-methyl)pyridinium chloride, Cetyl dimethyl ethyl ammonium bromide, Lauryl pyridinium chloride, Cetyl ethyl dimethyl ammonium bromide, Tridecyl benzyl hydroxy ethyl imidazolinium chloride, Dodecyl acetamido dimethyl 15. benzyl ammonium chloride, Polyalkyl naphthalene methyl pyridinium chloride, Dialkyl dimethyl ammonium chloride, Dialkyl

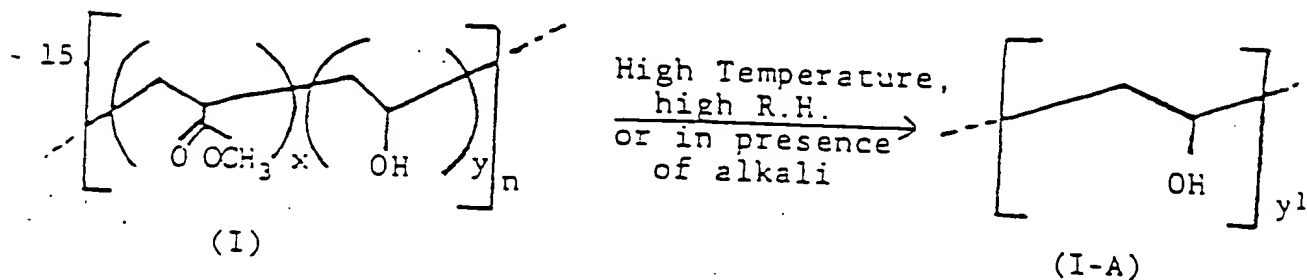
- dimethyl ammonium bromide, Dialkyl dimethyl ammonium bromide, Myristamido propyldimethyl benzyl ammonium chloride, Myristyl-Y-picolinium chloride, N-N-N'-N' 20. tetra methyl-N-N'-didodecyl- -hydroxy-propylene di-ammonium bromide, benzalkonium quaternary compounds, (6) halogenated salicylanilides, hexachlorophene, neomycin sulphate, bi-thionol, and 3,4,4'-trichloro- 25. carbanilide.

Although not wishing to be bound by any particular theory, it is believed that the improved aging characteristics of the water soluble films of this invention result from the high molecular compatibility between

30. the partially hydrolyzed polyvinyl acetate and polyacrylic acid, and more particularly, because of the ability of the polyacrylic acid to interfere with the inherent tendency of the partially hydrolyzed polyvinyl acetate to undergo further hydrolyzation

- (e.g. 96% or more) and become insoluble. This protective mechanism appears to be a preferential H-bonding of the partially hydrolyzed polyvinyl acetate with carbonyl sites from the polyacrylic acid. This, it is surmised, is made possible because of the compatibility of the two polymers, viz, the polyacrylic acid fits into the molecular lattice of the partially hydrolyzed polyvinyl acetate and, thus, prevents further crystallization by spoiling the molecular symmetry or perfection.

On a molecular scale, hydrolysis of partially hydrolyzed polyvinyl acetate can be represented by the following formula:



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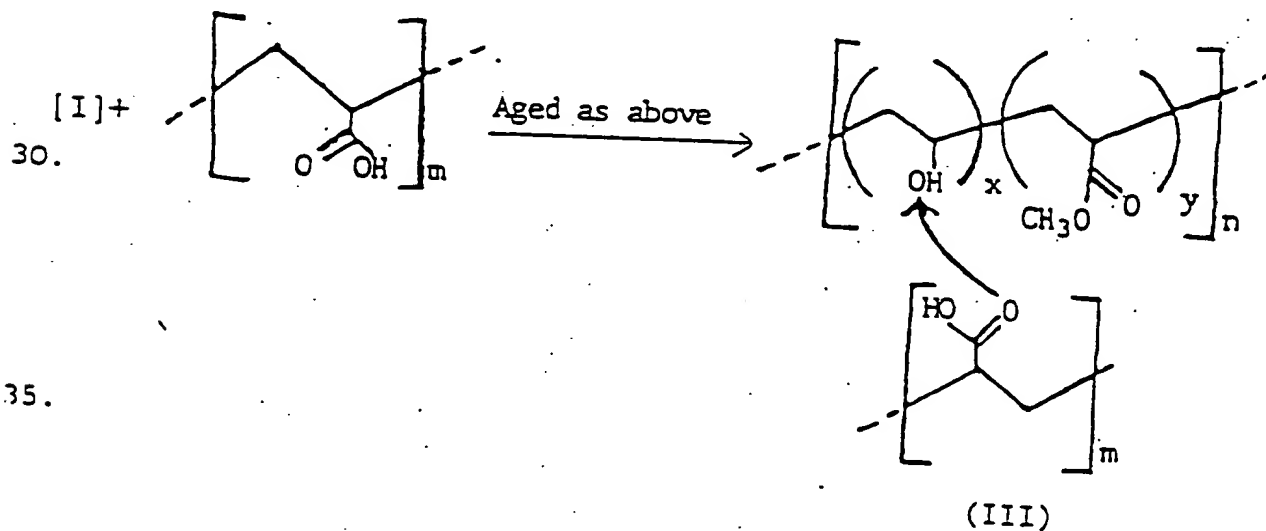
$$x \approx 5 \text{ to } 20 \text{ mole\%}$$

$$y \approx 80 \text{ to } 95 \text{ mole\%}$$

$$y^1 \approx 96 \text{ to } 99 \text{ mole\%}$$

- The mechanism of aging stabilization against further hydrolysis can be represented by the following

25. formula:



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- where formula (III) shows the interference H-bonding between the polyacrylic acid and partially hydrolyzed polyvinyl acetate. The hydrogen bonded structure (III) interferes sterically and electronically with continuing hydrolysis (as well as internal H-bonding) of the partially hydrolyzed polyvinyl acetate (I) which thereby prevents the conformational perfection of structure (I-A) which would result in high order crystallinity and insolubilization.
5. In any case, by whatever mechanism, it has been found that the water soluble films of this invention exhibit superior resistance to aging in low temperature/low humidity and high temperature/high humidity conditions, i.e., remain more soluble in cold water, have less tendency to become soft or tacky, and retain higher mechanical strength, as compared to conventional water soluble films based on partially hydrolysed polyvinyl acetate.
 10. The water soluble films are heat sealable and are readily formed into packages. Thus according to a further aspect of the invention there is provided a package containing a dry solid water-soluble or -dispersible material and formed from a film as described above. To make such a package two sheets of water soluble films can be placed one over the other and heat sealed along three edges. A dry, water soluble commodity, e.g. dry laundry powder, can be loaded into the package through the remaining open edge which can then also be heat sealed. It is a particular advantage of the invention that even after storage of the water soluble films for extended periods at low temperature/low humidity and/or high temperature/high humidity conditions, the heat sealability of the films is not adversely affected. Elasticity, strength, and clarity as well
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as high rate of solubility of the films are also maintained even in ice cold water conditions.

5. The invention may be put into practice in various ways and a number of specific embodiments will be described by way of example to illustrate the invention with reference to the following examples in which all "parts" and "percents" are "by weight" unless otherwise noted.

10. EXAMPLE 1

15. An aqueous casting solution was prepared by first forming a 10.0% solids solution of 88% hydrolysed polyvinylacetate (molecular weight in the range of 22,000 to 31,000) by forming a dispersion of the polymer in cold water, adding about 0.1% of nonionic anti-foaming agent (Triton CF-32) to the dispersion, and then bringing the polymer into solution by heating the dispersion to a temperature of 180°F to 220°F (82 to 93°C) with vigorous stirring. To eighty parts of this partially hydrolyzed polyvinyl acetate solution (10% solids), 2.5 parts of tetraethylene glycol plasticizers was added. Eight parts of a commercially available aqueous solution (25% solids) of polyacrylic acid (ACRYSOL A-3 (Trade Mark), molecular weight 25. 150,000) was added to the plasticized polyvinyl alcohol solution. The resulting casting solution was adjusted to 100 parts with water (9.5 parts water) to form an aqueous casting solution containing 12.5 parts (12.5%) of active ingredients, i.e., polymers and plasticizer. To this casting solution, about 0.5% biocide/preservative (GIV-GARD DXN, a product of Givudan Corp.) based on the amount of partially hydrolyzed polyvinyl acetate solids, was added. All ingredients were 30.

blended using vigorous agitation to assure homogeneity.

- From the aqueous casting solution films were prepared with both a 4-inch and 8-inch Gardener film casting knife using a blade clearance of 22-24 mils (0.56 to 0.61 mms). The casting solution was deposited on either mylar or plasticized polyvinyl chloride sheets as the casting surface. After drying in air overnight, clear films were obtained having a
5. thickness of 0.0015 inches (0.038 mms).
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EXAMPLE 2

- Example 1 was repeated except that 3.35 parts of polyglycerol (75% solids) were used as plasticizer in place of 2.4 parts of tetraethylene glycol and the amount of water was adjusted from 9.5 parts to 8.65 parts to again give a casting solution with 12.5% of active solids.
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CLAIMS:

1. A water soluble clear transparent coherent self supporting film suitable for use in packaging comprising a uniform homogeneous mixture of water soluble partially hydrolyzed polyvinyl acetate and polyacrylic acid
5. 2. A water soluble film as claimed in Claim 1 in which the weight ratio of partially hydrolyzed polyvinyl acetate to polyacrylic acid is in the range of from 10:1 to 1:1.
10. 3. A water soluble film as claimed in Claim 2 in which the weight ratio is about 4:1.
15. 4. A water soluble film as claimed in Claim 2 or 3 in which the partially hydrolyzed polyvinyl acetate has a degree of hydrolysis in the range of from 85% to 90% and a weight average molecular weight in the range of from 10,000 to 50,000 and the polyacrylic acid has a molecular weight in the range of from 30,000
20. to 400,000.
25. 5. A water soluble film as claimed in any one of Claims 1 to 4, in which the partially hydrolyzed polyvinyl acetate has a degree of hydrolysis in the range of from 86 to 89% and a weight average molecular weight in the range of from 22,000 to 31,000 and the polyacrylic acid has a molecular weight in the range of from 100,000 to 200,000.
30. 6. A water soluble film as claimed in any one of Claims 1 to 5 which further comprises a

plasticizer for the partially hydrolysed polyvinyl acetate component.

5. 7. A water soluble film as claimed in Claim 6 in which the plasticizer is tetraethylene glycol or polyglycerol.
10. 8. A water soluble film as claimed in any one of Claims 1 to 7 formed from an aqueous polymer solution comprising partially hydrolyzed polyvinyl acetate and polyacrylic acid, in which solution the total concentration of partially hydrolyzed polyvinyl acetate and polyacrylic acid is in the range 5% to 30%.
15. 9. A water soluble film as claimed in Claim 8 in which the said total concentration is in the range 8% to 20%.
20. 10. A water soluble film as claimed in any one of the preceding claims formed from an aqueous polymer solution comprising partially hydrolyzed polyvinyl acetate and polyacrylic acid, in which solution the weight ratio of partially hydrolyzed polyvinyl acetate to polyacrylic acid (on a dry weight basis) is in the range 10:1 to 1:1.
25. 11. A water soluble film as claimed in any one of the preceding claims formed from an aqueous polymer solution comprising partially hydrolyzed polyvinyl acetate and polyacrylic acid, the solution containing 0.5 to 5% by weight of the solution of a plasticizer for the partially hydrolyzed polyvinyl acetate.
30. 12. A water soluble film as claimed in any
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one of the preceding claims formed from an aqueous polymer solution comprising partially hydrolyzed polyvinyl acetate and polyacrylic acid, the solution containing up to 0.1% of a biocide, non-toxic to humans, based on the dry weight of the partially hydrolyzed polyvinyl acetate.

13. A water soluble film suitable for use in packaging prepared substantially as specifically described herein with reference to Example 1 or Example 2.

14. A process for making a water soluble plastics film suitable for use in packaging which comprises casting a continuous layer or film of an aqueous polymer solution comprising partially hydrolyzed polyvinyl acetate and polyacrylic acid on a temporary support removing the water therefrom to produce a continuous polymer film and stripping the film from the temporary support.

15. A process as claimed in Claim 14 substantially as specifically described herein with reference to Example 1 or Example 2.

16. A water soluble polymer film whenever made by a process as claimed in Claim 14 or Claim 15.

17. A package containing a dry solid water-soluble or -dispersible material and formed from a film as claimed in any one of Claims 1 to 13 and 16.
